

## **Patent Application**

### **NOVEL METHODS AND COMPOSITIONS FOR IMPROVED ELECTROPHORETIC DISPLAY PERFORMANCE**

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# **NOVEL METHODS AND COMPOSITIONS FOR IMPROVED ELECTROPHORETIC DISPLAY PERFORMANCE**

## **CROSS-REFERENCE TO RELATED APPLICATION**

**[0001]** This application claims the benefit of U.S. Provisional Application Serial No. 60/396,680, filed July 17, 2002, the content of which is incorporated herein by reference in its entirety.

## **BACKGROUND OF THE INVENTION**

### **Field of the Invention**

**[0002]** The invention is directed to novel methods and compositions useful for improving the performance of electrophoretic displays.

### **Description of Related Art**

**[0003]** The electrophoretic display (EPD) is a non-emissive device based on the electrophoresis phenomenon of charged pigment particles suspended in a solvent. It was first proposed in 1969. The display usually comprises two plates with electrodes placed opposing each other, separated by spacers. One of the electrodes is usually transparent. An electrophoretic fluid composed of a colored solvent with charged pigment particles dispersed therein is enclosed between the two plates. When a voltage difference is imposed between the two electrodes, the pigment particles migrate to one side or the other causing either the color of the pigment particles or the color of the solvent being seen from the viewing side.

**[0004]** There are several different types of EPDs. In the partition type EPD (see M.A. Hopper and V. Novotny, *IEEE Trans. Electr. Dev.*, 26(8):1148-1152 (1979)), there are partitions between the two electrodes for dividing the space into smaller cells in order to prevent undesired movement of particles, such as sedimentation. The microcapsule type EPD (as described in US Patent

Nos. 5,961,804 and 5,930,026) has a substantially two dimensional arrangement of microcapsules each having therein an electrophoretic composition of a dielectric fluid and a suspension of charged pigment particles that visually contrast with the dielectric solvent. Another type of EPD (see US Patent No. 3,612,758) has electrophoretic cells that are formed from parallel line reservoirs. The channel-like electrophoretic cells are covered with, and in electrical contact with, transparent conductors. A layer of transparent glass from which side the panel is viewed overlies the transparent conductors.

**[0005]** An improved EPD technology was disclosed in co-pending applications, US Serial Number 09/518,488, filed on March 3, 2000 (corresponding to WO 01/67170), US Serial Number 09/606,654, filed on June 28, 2000 (corresponding to WO 02/01281) and US Serial Number 09/784,972, filed on February 15, 2001 (corresponding to WO02/65215), all of which are incorporated herein by reference. The improved EPD cells are prepared by microembossing a layer of thermoplastic or thermoset resin composition coated on a first substrate layer to form the microcups of well-defined shape, size and aspect ratio. The microcups are then filled with an electrophoretic fluid and sealed with a sealing layer. A second substrate layer is laminated over the filled and sealed microcups, preferably with an adhesive layer.

**[0006]** To reduce irreversible electrodeposition of dispersion particles or other charged species onto the electrodes (such as ITO), a thin protection or release layer may be coated on the electrodes. The protective layer improves the performance of the display, including an increase in display image uniformity and longevity. In addition, a faster electro-optical response has been observed in displays with a protective layer.

**[0007]** However, the thin protective layer method also has disadvantages. For example, the use of a protection or release layer on electrodes tends to result in deterioration in contrast ratio and bi-stability of the EPD. A higher  $D_{min}$  (or a

lower degree of whiteness or % reflectance) in the background particularly at low driving voltages is also typically observed in EPDs with coated electrodes.

**[0008]** Accordingly, there is a need for more effective methods to improve the response rate and image uniformity and also to reduce irreversible electrodeposition of dispersion particles or other charged species onto the electrodes.

### **SUMMARY OF THE INVENTION**

**[0009]** The present invention relates to novel methods and compositions for improving the performance of an electrophoretic display.

**[0010]** The first aspect of the present invention is directed to a method for improving the performance of an electrophoretic display, which method comprises adding a high absorbance dye or pigment to at least one electrode protecting layer in the display.

**[0011]** The second aspect of the present invention is directed to a method for improving the performance of an electrophoretic display, which method comprises adding conductive particles to at least one electrode protecting layer in the display.

**[0012]** The third aspect of the present invention is directed to a method for improving the performance of an electrophoretic display, which method comprises adding a charge transport material to at least one electrode protecting layer in the display.

**[0013]** The fourth aspect of the present invention is directed to an adhesive composition comprising an adhesive material and a high absorbance dye or pigment, or conductive particles or a charge transport material.

**[0014]** The fifth aspect of the present invention is directed to a sealing composition comprising a polymeric material and a high absorbance dye or pigment, or conductive particles or a charge transport material.

**[0015]** The sixth aspect of the present invention is directed to a primer layer composition comprising a thermoplastic, thermoset or a precursor thereof and a high absorbance dye or pigment, or conductive particles or a charge transport material.

**[0016]** The adhesive, sealing and primer layer compositions of the present invention are particularly useful for electrophoretic displays prepared by the microcup technology.

**[0017]** The seventh aspect of the present invention is directed to the use of a high absorbance dye or pigment, or conductive particles, or a charge transport material or a combination thereof for improving performance of an electrophoretic display.

**[0018]** The eighth aspect of the present invention is directed to an electrophoretic display comprising at least one electrode protecting layer formed of a composition comprising a high absorbance dye or pigment, or conductive particles, or a charge transport material or a combination thereof.

**[0019]** The electrophoretic displays of the present invention show an increase in contrast ratio and image bistability even at low driving voltages without trade-off in display longevity and image uniformity.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

**[0020]** Figures 1A and 1B are schematic depiction of an electrophoretic display cell prepared by the microcup technology.

## **DETAILED DESCRIPTION OF THE INVENTION**

### **Definitions**

**[0021]** Unless defined otherwise in this specification, all technical terms are used herein according to their conventional definitions as they are commonly used and understood by those of ordinary skill in the art.

**[0022]** The term "microcup" refers to the cup-like indentations which may be created by methods such as microembossing or a photolithographic process as described in the co-pending application, US Serial No. 09/518,488.

**[0023]** The term "well-defined", when describing the microcups or cells, is intended to indicate that the microcup or cell has a definite shape, size and aspect ratio which are pre-determined according to the specific parameters of the manufacturing process.

**[0024]** The term "aspect ratio" is a commonly known term in the art of electrophoretic displays. In this application, it refers to the depth to width or depth to length ratio of the microcups.

**[0025]** The term "Dmax" refers to the maximum achievable optical density of the display.

**[0026]** The term "Dmin" refers to the minimum optical density of the display background.

**[0027]** The term "contrast ratio" refers to the ratio of the reflectance (% of light reflected) of the Dmin state to the reflectance of the Dmax state.

**[0028]** The term "charge transport material" is defined as a material capable of transporting either electrons or holes from one side (such as the electrode side) of the protecting layer to the other side (such as the electrophoretic fluid side) or

vis-versa. Electrons are injected from the cathode and holes are injected from the anode into the electron transporting and hole transporting layer, respectively. A general review of the charge transport materials may be found in references, such as P.M. Bosenberger and D.S. Weiss, "Photoreceptors: Organic Photoconductors" in "Handbook of Imaging Materials", A.S. Diamond ed., pp379, (1991), Marcel Dekker, Inc.; H. Sher and EW Montroll, Phys. Rev., B12, 2455 (1975); S.A. Van Slyke et.al., Appl. Phys. Lett., 69, 2160, (1996); or F. Nuesch et.al., J. Appl. Phys., 87, 7973 (2000).

**[0029]** The term "electrode protecting layer" is defined in the section below.

#### **General Description of the Microcup Technology**

**[0030]** Figures 1A and 1B depict typical display cells prepared by the microcup technology as disclosed in WO01/67170. The microcup based display cell (10) is sandwiched between a first electrode layer (11) and a second electrode layer (12). A thin protective layer (13) is optionally present between the cell (10) and the second electrode layer (12) as seen in the figures. As shown in Figure 1A, the layer (13) may be a primer layer (adhesion promoting layer) to improve the adhesion between the microcup material and the second electrode layer (12). Alternatively the layer (13) may be a thin layer of the microcup material (as shown in Figure 1B) if the microcup array is prepared by an embossing process. The cell (10) is filled with an electrophoretic fluid and sealed with a sealing layer (14) on the open side of the microcups. The first electrode layer (11) is laminated onto the sealed cell, preferably with an adhesive (15).

**[0031]** In the context of the present invention, the term "electrode protecting layer" may be the primer layer or the thin microcup layer (13), sealing layer (14) or adhesive layer (15) as shown in Figures 1A and 1B.

**[0032]** In case of in-plane switching EPDs, one of the electrode layers (11 or 12) may be replaced by an insulating layer.

**[0033]** The display panel may be prepared by microembossing or photolithography as disclosed in WO01/67170. In the microembossing process, an embossable composition is coated onto the conductor side of the second electrode layer (12) and embossed under pressure to produce the microcup array. To improve the mold release property, the conductor layer may be pretreated with a thin primer layer (13) before coating the embossable composition.

**[0034]** The embossable composition may comprise a thermoplastic or thermoset material or a precursor thereof, such as multifunctional vinyls including but are not limited to, acrylates, methacrylates, allyls, vinylbenzenes, vinyl ethers, multifunctional epoxides and oligomers or polymers thereof and the like. Multifunctional acrylate and oligomers thereof are the most preferred. A combination of a multifunctional epoxide and a multifunctional acrylate is also very useful to achieve desirable physico-mechanical properties. A low T<sub>g</sub> binder or crosslinkable oligomer imparting flexibility, such as urethane acrylate or polyester acrylate, is usually also added to improve the flexure resistance of the embossed microcups. The composition may contain an oligomer, a monomer, additives and optionally a polymer. The T<sub>g</sub> (glass transition temperature) for the embossable composition usually ranges from about -70°C to about 150°C, preferably from about -20°C to about 50°C.

**[0035]** The microembossing process is typically carried out at a temperature higher than the T<sub>g</sub>. A heated male mold or a heated housing against which the mold presses may be used to control the microembossing temperature and pressure.

**[0036]** The mold is released during or after the embossable composition is hardened to reveal an array of microcups (10). The hardening of the embossable



composition may be accomplished by cooling, solvent evaporation, cross-linking by radiation, heat or moisture. If the curing of the embossable composition is accomplished by UV radiation, UV may radiate onto the embossable composition through the transparent conductor layer. Alternatively, UV lamps may be placed inside the mold. In this case, the mold must be transparent to allow the UV light to radiate through the pre-patterned male mold on to the embossable composition.

**[0037]** The composition of the primer layer is at least partially compatible with the embossing composition or the microcup material after curing. In practice, it may be the same as the embossing composition.

**[0038]** In general, the dimension of each individual microcup may be in the range of about  $10^2$  to about  $1 \times 10^6 \mu\text{m}^2$ , preferably from about  $10^3$  to about  $1 \times 10^5 \mu\text{m}^2$ . The depth of the microcups is in the range of about 3 to about 100 microns, preferably from about 10 to about 50 microns. The ratio between the area of opening to the total area is in the range of from about 0.05 to about 0.95, preferably from about 0.4 to about 0.9. The width of the openings usually are in the range of from about 15 to about 450 microns, preferably from about 25 to about 300 microns from edge to edge of the openings.

**[0039]** The microcups are then filled with an electrophoretic fluid and sealed as disclosed in co-pending applications, US Serial Number 09/518,488, filed on March 3, 2000 (corresponding to WO 01/67170), US Serial Number 09/759,212, filed on January 11, 2001 (corresponding to WO02/56097), US Serial Number 09/606,654, filed on June 28, 2000 (corresponding to WO 02/01281) and US Serial Number 09/784,972, filed on February 15, 2001 (corresponding to WO02/65215), all of which are incorporated herein by reference.

**[0040]** The sealing of the microcups may be accomplished in a number of ways. Preferably, it is accomplished by overcoating the filled microcups with a sealing composition comprising a solvent and a sealing material selected from the

group consisting of thermoplastic elastomers, polyvalent acrylate or methacrylate, cyanoacrylates, polyvalent vinyl including vinylbenzene, vinylsilane, vinyl ether, polyvalent epoxide, polyvalent isocyanate, polyvalent allyl, oligomers or polymers containing crosslinkable functional groups and the like. Additives such as a polymeric binder or thickener, photoinitiator, catalyst, vulcanizer, filler, colorant or surfactant may be added to the sealing composition to improve the physico-mechanical properties and the optical properties of the display. The sealing composition is incompatible with the electrophoretic fluid and has a specific gravity no greater than that of the electrophoretic fluid. Upon solvent evaporation, the sealing composition forms a conforming seamless seal on top of the filled microcups. The sealing layer may be further hardened by heat, radiation or other curing methods. Sealing with a composition comprising a thermoplastic elastomer is particularly preferred. Examples of thermoplastic elastomers may include, but are not limited to, tri-block or di-block copolymers of styrene and isoprene, butadiene or ethylene/butylene, such as the Kraton™ D and G series from Kraton Polymer Company. Crystalline rubbers such as poly(ethylene-co-propylene-co-5-methylene-2-norbornene) and other EPDM (Ethylene Propylene Diene Rubber terpolymer) from Exxon Mobil have also been found very useful.

**[0041]** Alternatively, the sealing composition may be dispersed into an electrophoretic fluid and filled into the microcups. The sealing composition is incompatible with the electrophoretic fluid and is lighter than the electrophoretic fluid. Upon phase separation, the sealing composition floats to the top of the filled microcups and forms a seamless sealing layer thereon after solvent evaporation. The sealing layer may be further hardened by heat, radiation or other curing methods.

**[0042]** The sealed microcups finally are laminated with the first electrode layer (11) which may be pre-coated with an adhesive layer (15).

**[0043]** Preferred materials for the adhesive layer may be formed from one adhesive or a mixture thereof selected from a group consisting of pressure sensitive, hot melt and radiation curable adhesives. The adhesive materials may include, but are not limited to, acrylics, styrene-butadiene copolymers, styrene-butadiene-styrene block copolymers, styrene-isoprene-styrene block copolymers, polyvinylbutyral, cellulose acetate butyrate, polyvinylpyrrolidone, polyurethanes, polyamides, ethylene-vinylacetate copolymers, epoxides, multifunctional acrylates, vinyls, vinyl ethers, and their oligomers, polymers and copolymers. Adhesives comprising polymers or oligomers having a high acid or base content such as polymers or copolymers derived from acrylic acid, methacrylic acid, itaconic acid, maleic anhydride, vinylpyridine and derivatives thereof are particularly useful. The adhesive layer may be post cured by, for example, heat or radiation such as UV after lamination.

#### **Embodiments of the Present Invention**

**[0044]** The term "electrode protecting layer", as stated above, may be the primer layer (13), sealing layer (14) or adhesive layer (15) as shown in Figures 1A and 1B.

**[0045]** The primer layer (13) of the display, as stated above, may be formed from a composition comprising a thermoplastic or thermoset material or a precursor thereof, such as a multifunctional acrylate or methacrylate, a vinylbenzene, a vinyl ether, an epoxide or an oligomers or polymer thereof. A multifunctional acrylate and oligomers thereof are usually preferred. The thickness of the primer layer is in the range of 0.1 to 5 microns, preferably 0.1-1 microns.

**[0046]** The sealing layer (14) is formed from a composition comprising a solvent and a material selected from the group consisting of thermoplastic elastomers, polyvalent acrylate or methacrylate, cyanoacrylates, polyvalent vinyl including vinylbenzene, vinylsilane, vinyl ether, polyvalent epoxide, polyvalent

isocyanate, polyvalent allyl, oligomers or polymers containing crosslinkable functional groups and the like. The thickness of the sealing layer is in the range of 0.5 to 15 microns, preferably 1 to 8 microns.

**[0047]** Materials suitable for the adhesive layer (15) may include, but are not limited to, acrylics, styrene-butadiene copolymers, styrene-butadiene-styrene block copolymers, styrene-isoprene-styrene block copolymers, polyvinylbutyral, cellulose acetate butyrate, polyvinylpyrrolidone, polyurethanes, polyamides, ethylene-vinylacetate copolymers, epoxides, multifunctional acrylates, vinyls, vinyl ethers, and their oligomers, polymers and copolymers. The thickness of the adhesive layer is in the range of 0.2 to 15 microns, preferably 1 to 8 microns.

**[0048]** The first aspect of the present invention is directed to a method for improving the performance of an electrophoretic display, which method comprises adding a high absorbance dye or pigment into at least one of the electrode protecting layers of the display. The dye or pigment may be dissolved or dispersed in the electrode protecting layer.

**[0049]** The dye or pigment may be present in more than one electrode protecting layers on the non-viewing side of the display. If the dye or pigment is used in the primer or the microcup layer, it should not interfere with the hardening or mold release in the microembossing process.

**[0050]** In addition to the improvement in switching performances, the use of a high absorbance dye or pigment in the layers opposite from the viewing side of the display also provides a dark background color and an enhanced contrast ratio.

**[0051]** The dye or pigment preferably has an absorption band in the range of 320-800 nm, more preferably 400-700 nm. Suitable dyes or pigments for the present invention may include, but are not limited to, metal phthalocyanines or naphthalocyanines (wherein the metal may be Cu, Al, Ti, Fe, Zn, Co, Cd, Mg, Sn,

Ni, In, Ti, V or Pb), metal porphines (wherein the metal may be Co, Ni or V), azo (such as diazo or polyazo) dyes, squaraine dyes, perylene dyes and croconine dyes. Other dyes or pigments which may generate or transport charge in their excited state or ground state would also be suitable. Examples of this type of dyes or pigments are those typically used as charge generating materials in organic photoconductors (See P.M. Bosenberger and D.S. Weiss, "Photoreceptors: Organic Photoconductors" in "Handbook of Imaging Materials", A.S. Diamond ed., pp379, (1991), Marcel Dekker, Inc).

**[0052]** Particularly preferred dyes or pigments are:

**[0053]** Cu phthalocyanines and naphthalocyanines such as Orasol™ Blue GN (C.I. Solvent Blue 67, Cu {29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32}-{{3-(1-methyethoxy)propyl}amino}sulfonyl derivative from Ciba Specialty Chemicals (High Point, NC);

**[0054]** Ni phthalocyanine;

**[0055]** Ti phthalocyanine;

**[0056]** Ni tetraphenylporphine;

**[0057]** Co phthalocyanine;

**[0058]** Metal porphine complexes such as tetraphenylporphine vanadium(IV) oxide complex and alkylated or alkoxylated derivatives thereof;

**[0059]** Orasol Black RLI (C.I. Solvent Black 29, 1:2 Chrome complex, from Ciba Specialty Chemicals);

**[0060]** Diazo or polyazo dyes including Sudan dyes such as Sudan Black B, Sudan Blue, Sudan R, Sudan Yellow or Sudan I-IV;

**[0061]** Squaraine and croconine dyes such as 1-(4-dimethylamino-pheny)-3-(4-dimethylimmonium-cyclohexa-2,5-dien-1-ylidene)-2-oxo-cyclobuten-4-olate, 1-(4-methyl-2-morpholino-selenazo-5-yl)-3-(2,5-dihydro-4-methy-2[morpholin-1-ylidene-onium]-selenzaol-5-ylidene)-2-oxo-cyclobuten-4-olate or 1-(2-dimethylamino-4-phenyl-thiazol-5-yl)-3-(2,5-dihydro-2-dimethylimmonium-4-phenyl)-thiazol-5-ylidene)-2-oxo-cyclobuten-4-olate; and

**[0062]** Condensed perylene dyes or pigments such as 2,9-di(2-hydroxyethyl)-anthra[2.1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetrone, 9-di(2-methoxyethyl)-anthra[2.1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetrone, bisimidazo[2,1-a:2',1'-a']anthra[2.1,9-def:6,5,10-d'e'f']diisoquinoline-dione or anthra[2",1",9":4,5,6:6",5",10":4',5',6']-diisoquinoline[2,1-a:2'1'-a]diperimidine-8,20-dione.

**[0063]** Some of the dyes or pigments such as metal (particularly Cu and Ti) phthalocyanines and naphthalocyanines have also been found useful as charge transport materials.

**[0064]** The concentration of the dye or pigment may range from about 0.1% to about 30%, preferably from about 2% to about 20%, by weight of the total solid content of the layer. Other additives such as surfactants, dispersion aids, thickeners, crosslinking agents, vulcanizers, nucleation agents or fillers may also be added to enhance the coating quality and display performance.

**[0065]** The second aspect of the invention is directed to a method for improving performance of an electrophoretic display, which method comprises adding particles of a conductive material into at least one of the electrode protecting layers.

**[0066]** The conductive materials include, but not limited to, organic conducting compounds or polymers, carbon black, carbonaceous particles,

graphite, metals, metal alloys or conductive metal oxides. Suitable metals include Au, Ag, Cu, Fe, Ni, In, Al and alloys thereof. Suitable metal oxides may include indium-tin-oxide (ITO), indium-zinc-oxide (IZO), antimony-tin oxide (ATO), barium titanate ( $\text{BaTiO}_3$ ) and the like. Suitable organic conducting compounds or polymers may include, but are not limited to, poly(p-phenylene vinylene), polyfluorene, poly(4,3-ethylenedioxythiophene), poly(1,2-bis-ethylthio-acetylene), poly(1,2-bis-benzylthio-acetylene), 5,6,5',6'-tetrahydro-[2,2']bi[1,3]dithiolo[4,5-b][1,4]dithiinyliene, 4,5,6,7,4',5',6',7'-octahydro-[2,2']bi[benzo[1,3]dithiolyliene, 4,4'-diphenyl-[2,2']bi[1,3]dithiolyliene, 2,2,2',2'-tetraphenyl-bi-thiapyran-4,4'-diylidene, hexakis-bezylthio-benzene and derivatives thereof.

**[0067]** Organic and inorganic particles overcoated with any of the above-mentioned conductive materials are also useful.

**[0068]** Addition of the conductive material, in the form of particles, into an electrode protecting layer improves the contrast ratio at low operating voltages. However, the amount of the conductive material added should be well controlled so that it does not cause short or current leakage. The amount of the conductive material added preferably is in the range of from about 0.1% to about 40%, more preferably from about 5% to about 30%, by weight of the total solid content of the layer.

**[0069]** Additives such as dispersion agents, surfactants, thickeners, crosslinking agents, vulcanizers or fillers may also be added to improve the coating quality and display performance. The conductive material may be added to more than one electrode protecting layers. The particle size of the conductive material is in the range of from about 0.01 to about 5  $\mu\text{m}$ , preferably from about 0.05 to about 2  $\mu\text{m}$ .

**[0070]** The third aspect of the invention is directed to a method for improving the performance of an electrophoretic display, which method comprises adding a

charge transport material to at least one of the electrode protecting layers of the display.

**[0071]** Charge transport materials are materials capable of transporting either electrons or holes from one side (such as the electrode side) of the electrode protecting layer to the other side (such as the electrophoretic fluid side) or vice-versa. Electrons are injected from the cathode and holes are injected from the anode into the electron transporting and hole transporting layers, respectively. A general review of the charge transport materials may be found in references, such as P.M. Bosenberger and D.S. Weiss, "Photoreceptors: Organic Photoconductors" in "Handbook of Imaging Materials", A.S. Diamond ed., pp379, (1991), Marcel Dekker, Inc.; H. Sher and EW Montroll, Phys. Rev., B12, 2455 (1975); S.A. Van Slyke et.al., Appl. Phys. Lett., 69, 2160, (1996); or F. Nuesch et.al., J. Appl. Phys., 87, 7973 (2000).

**[0072]** Suitable electron and hole transport materials may be found from general technical reviews in organic photoconductors and organic light emitting diodes such as those listed above.

**[0073]** The hole transport materials are typically compounds having a low ionization potential which may be estimated from their solution oxidation potentials. In the context of the present invention, compounds having an oxidation potential less than 1.4 V, particularly less than 0.9 V (vs SCE) are found useful as the charge transport materials. Suitable charge transport materials should also have acceptable chemical and electrochemical stability, reversible redox behavior and sufficient solubility in the protection layer for the electrodes. Too low an oxidation potential may result in undesirable oxidation in air and a short display shelf life. Compounds having oxidation potentials between 0.5-0.9 V (vs SCE) are found particularly useful for this invention.



**[0074]** In the context of the present invention, particularly useful hole transport materials include compounds in the general classes of:

**[0075]** Pyrazolines such as 1-phenyl-3-(4'-dialkylaminostyryl)-5-(4"-dialkylaminophenyl)pyrazoline;

**[0076]** Hydrazones such as p-dialkylaminobenzaldehyde-N,N-diphenylhydrazone, 9-ethyl-carbazole-3-aldehyde-N-methyl-N-phenylhydrazone, pyrene-3-aldehyde-N,N-diphenylhydrazone, 4-diphenylamino-benzaldehyde-N,N-diphenylhydrazone, 4-N,N-bis(4-methylphenyl)-amino-benzaldehyde-N,N-diphenylhydrazone, 4-dibenzylamino-benzaldehyde-N,N-diphenylhydrazone or 4-dibenzylamino-2-methyl-benzaldehyde-N,N-diphenylhydrazone;

**[0077]** Oxazoles and oxadiazoles such as 2,5-bis-(4-dialkylaminophenyl)-4-(2-chlorophenyl)oxazole, 2,5-bis-(4-N,N'-dialkylaminophenyl)-1,3,4-oxadiazole, 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,2,3-oxadiazole, 2,2'-(1,3-phenylene)bis[5-[4-(1,1-dimethylethyl)phenyl]1,3,4-oxadiazole, 2,5-bis(4-methylphenyl)-1,3,4-oxadiazole or 1,3-bis(4-(4-diphenylamino)-phenyl-1,3,4-oxadiazol-2-yl)benzene;

**[0078]** Enamines, carbazoles or arylamines, particularly triarylamines such as bis(p-ethoxyphenyl)acetaldehyde di-p-methoxyphenylamine enamine, N-alkylcarbazole, trans-1,2-biscarbazoyl-cyclobutane, 4,4'-bis(carbazol-9-yl)-biphenyl, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1-bi[phenyl]-4,4'-diamine, 4,4'-bis(N-naphthyl-N-phenyl-amino)biphenyl (or N,N'-di(naphthalene-2-yl)-N,N'-diphenyl-benzidine); 4,4',4"-trismethyl-triphenylamine, N-biphenyl-N-phenyl-N-(3-methylphenyl)amine, 4-(2,2-bisphenyl-ethen-1-yl)triphenylamine, N,N'-di-(4-methylphenyl)N,N'-diphenyl-1,4-phenyldiamine, 4-(2,2-bisphenyl-ethen-1-yl)-4',4"-dimethyl-triphenylamine, N,N,N',N'-tetraphenylbenzidine, N,N,N',N'-tetrakis(4-methylphenyl)-benzidine, N,N'-bis-(4-methylphenyl)-N,N'-bis-(phenyl)-benzidine, 4,4'-bis(dibenz-azepin-1-yl)biphenyl; 4,4'-bis(dihydro-dibenz-azepin-1-yl)-biphenyl, di-(4-dibenzylamino-phenyl)-ether, 1,1-bis-(4-bis(4-methyl-phenyl)-amino-

phenyl)cyclohexane, 4,4'-bis(N,N-diphenylamino)-quaterphenyl, N,N,N',N'-tetrakis(naphtha-2-yl)benzidine, N,N'-bis(phenanthren-9-yl)-N,N'-bis-phenylbenzidine, N,N'-bis(phenanthren-9-yl)-N,N'-bis-phenyl-benzidine, 4,4',4''-tris(carbazol-9-yl)-triphenylamine, 4,4',4''-tris(N,N-diphenylamino)-triphenylamine, 4,4'-bis(N-(1-naphthyl)-N-phenyl-amino)-quaterphenyl, 4,4',4''-tris(N-(1-naphthyl)-N-phenyl-amino) triphenylamine or N,N'-diphenyl-N,N'-bis(4'-(N,N-bis(naphthy-1-yl)-amino)-biphenyl-4-yl)-benzidine;

**[0079]** Triarylmethanes such as bis(4-N,N-dialkylamino-2-methylphenyl)-phenylmethane;

**[0080]** Biphenyls such as 4,4'-bis(2,2-diphenyl-ethen-1-yl)-biphenyl;

**[0081]** Dienes and dienones such as 1,1,4,4-tetraphenyl-butadiene, 4,4'-(1,2-ethanediylidene)-bis(2,6-dimethyl-2,5-cyclohexadien-1-one), 2-(1,1-dimethylethyl)-4-[3-(1,1-dimethylethyl)-5-methyl-4-ox-2,5-cyclohexa-dien-1-ylidene]-6-methy-2,5-cyclohexadien-1-one, 2,6-bis(1,1-dimethylethyl)4-[3,5-bis(1,1-dimethylethyl)4-oxo-2,5-cyclohexa-dien-1-ylidene]-2,5-cyclohexadien-1-one or 4,4'-(1,2-ethanediylidene)-bis(2,6-(1,1-dimethyl-ethyl)2,5-cyclohexadien-1-one); and

**[0082]** Triazoles such as 3,5-bis(4-tert-phenyl)-4-phenyl-triazole or 3-(4-biphenylyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole.

**[0083]** Oligomeric or polymeric derivatives containing any of the above-mentioned functional groups are also useful as charge transport materials.

**[0084]** Particularly useful electron transport materials include electron deficient compounds in the general classes of:

**[0085]** Fluorenones such as 2,4,7-trinitro-9-fluorenone or 2-(1,1-dimethylbutyl)-4,5,7-trinitro-9-fluorenone; and

**[0086]** Nitriles such as (4-butoxycarbonyl-9-fluorenylidene)malononitrile, 2,6-di-tert-butyl-4-dicyanomethylene-4-H-thiopyran-1,1-dioxide, 2-(4-(1-methyl-ethyl)-phenyl)-6-phenyl-4H-thiopyran-4-ylidene]-propanedinitril-1,1-dioxide or 2-phenyl-6-methylphenyl-4-dicyanomethylene-4-H-thiopyran-1,1-dioxide or 7,7,8,8-tetrachcyanonquinodimethane.

**[0087]** The oligomeric or polymeric derivatives containing any of the above-mentioned functional groups are also useful.

**[0088]** The hole and electron transfer materials may be co-present in the same layer or even in the same molecule or in different layers on opposite or the same side of the display cell. Dopants and host materials such as 4-(dicyanomethylene)-2-methyl-6-(julolidin-4-yl-vinyl)-4H-pyran, bis(2-(2-hydroxyphenyl)-benz-1,3-thiazolato)-Zn complex, bis(2-(2-hydroxyphenyl)-benz-1,3-oxadiazoleato)-Zn complex, tris(8-hydroxy-chinolinato)-Al complex, tris(8-hydroxy-4-methyl-chinolinato)-Al complex or tris(5-chloro-8-hydroxy-chinolinato)-Al complex may also be added into the electrode protecting layer.

**[0089]** The charge transport material may be incorporated into the composition of one electrode protecting layer or may be present in more than one layers. A clear and colorless charge transport material is preferred if it is to be added into the electrode protecting layer on the viewing side of the display. The concentration of the charge transport material may range from about 0.1% to about 30%, preferably from about 2% to about 20%, by weight of the total solid content of the layer. Other additives such as surfactants, dispersion aids, thickeners, crosslinking agents, vulcanizers, nucleation agents or fillers may also be added to enhance the coating quality and display performance.

**[0090]** It should be noted that the three aspects of the invention may be performed alone or in combination. More than one aspect of the invention may also be co-present in the same layer. The materials used in the electrode

protecting layer on the viewing side of the display are preferred to be colorless and transparent. Also, the materials used in the primer and the microcup layers should not interfere with the hardening (such as UV curing) of the layers or mold release in the embossing process.

**[0091]** The fourth aspect of the present invention is directed to an adhesive composition comprising an adhesive material and a high absorbance dye or pigment, or an adhesive material and conductive particles, or an adhesive material and a charge transport material, or an adhesive material and a combination of two or more selected from a high absorbance dye or pigment, conductive particles or a charge transport material.

**[0092]** The fifth aspect of the present invention is directed to a sealing composition comprising a polymeric material and a high absorbance dye or pigment, or a polymeric material and conductive particles, or a polymeric material and a charge transport material, or a polymeric material and a combination of two or more selected from a high absorbance dye or pigment, conductive particles or a charge transport material.

**[0093]** The sixth aspect of the present invention is directed to a primer layer composition comprising a thermoplastic, thermoset or a precursor thereof and a high absorbance dye or pigment, or a thermoplastic, thermoset or a precursor thereof and conductive particles, or a thermoplastic, thermoset or a precursor thereof and a charge transport material, or a thermoplastic, thermoset or a precursor thereof and a combination of two or more selected from a high absorbance dye or pigment, conductive particles or a charge transport material.

**[0094]** The sealing, adhesive and primer layer compositions are particularly useful for electrophoretic displays prepared from the microcup technology.

**[0095]** Suitable adhesive materials, sealing materials, primer materials, thermoplastic or thermoset materials, high absorbance dyes or pigments, conductive particles and charge transport materials used in the compositions have all been described in this application.

**[0096]** The seventh aspect of the present invention is directed to the use of a high absorbance dye or pigment, conductive particles, a charge transport material or a combination thereof for improving performance of an electrophoretic display.

**[0097]** The eighth aspect of the present invention is directed to an electrophoretic display comprising at least one electrode protecting layer formed of a composition comprising a high absorbance dye or pigment, or conductive particles, or a charge transport material or a combination thereof.

**[0098]** While the microcup technology as disclosed in WO01/67170 is discussed in this application, it is understood that the methods, compositions and uses of the present invention are applicable to all types of electrophoretic displays, including but not limited to, the microcup-based displays (WO01/67170), the partition type displays (see M.A. Hopper and V. Novotny, *IEEE Trans. Electr. Dev.*, 26(8):1148-1152 (1979)), the microcapsule type displays (US Patent Nos. 5,961,804 and 5,930,026) and the microchannel type displays (US Patent No. 3,612,758).

### **EXAMPLES**

**[0099]** The following examples are given to enable those skilled in the art to more clearly understand and to practice the present invention. They should not be considered as limiting the scope of the invention, but merely as being illustrative and representative thereof.

## **Comparative Example 1**

### **Example 1A:**

#### **Preparation of Primer Coated Transparent Conductor Film**

[0100] A primer coating solution containing 33.2 gm of EB 600™ (UCB, Smyrna, GA), 16.12 gm of SR 399™ (Sartomer, Exton, PA), 16.12 gm of TMPTA (UCB, Smyrna, GA), 20.61 gm of HDODA (UCB, Smyrna, GA), 2 gm of Irgacure™ 369 (Ciba, Tarrytown, NY), 0.1 gm of Irganox™ 1035 (Ciba), 44.35 gm of poly(ethyl methacrylate) (MW. 515,000, Aldrich, Milwaukee, WI) and 399.15 gm of MEK (methyl ethyl ketone) was mixed thoroughly and coated onto a 3 mil transparent conductor film (ITO/PET film, 5 mil OC50 from CPFilms, Martinsville, VA) using a #4 wire bar. The coated ITO film was dried in an oven at 65°C for 10 minutes, then exposed to 1.8 J/cm<sup>2</sup> of UV light under nitrogen using a UV conveyer (DDU, Los Angeles, CA).

### **Example 1B:**

#### **Preparation of Microcups**

**Table 1. Microcup Composition**

Component	Weight Part	Source
EB 600	33.15	UCB
SR 399	32.24	Sartomer
HDODA	20.61	UCB
EB1360	6.00	UCB
Hycar X43	8.00	BF Goodrich
Irgacure 369	0.20	Ciba
ITX	0.04	Aldrich
Antioxidant Ir1035	0.10	Ciba

[0101] 33.15 Gm of EB 600™ (UCB, Smyrna, GA), 32.24 gm of SR 399™ (Sartomer, Exton, PA), 6.00 gm of EB1360™ (UCB, Smyrna, GA), 8 gm of Hycar 1300x43 (reactive liquid polymer, Noveon Inc. Cleveland, OH), 0.2 gm of Irgacure™ 369 (Ciba, Tarrytown, NY), 0.04 gram of ITX (Isopropyl-9H-thioxanthen-

9-one, Aldrich, Milwaukee, WI), 0.1 gm of Irganox™ 1035 (Ciba, Tarrytown, NY) and 20.61 gram of HDDA (1,6-hexanediol diacrylate, UCB, Smyrna, GA) were mixed thoroughly with a Stir-Pak mixer (Cole Parmer, Vernon, IL) at room temperature for about 1 hour, and degassed by centrifuge at 2000 rpm for about 15 minutes.

[0102] The microcup composition was slowly coated onto a 4"x4" electroformed Ni male mold for an array of 72  $\mu\text{m}$  (length) x 72  $\mu\text{m}$  (width) x 35  $\mu\text{m}$  (depth) x 13  $\mu\text{m}$  (width of top surface of spacing between cups) microcups. A plastic blade was used to remove excess of fluid and gently squeeze it into "valleys" of the Ni mold. The coated Ni mold was heated in an oven at 65°C for 5 minutes and laminated with the primer coated ITO/PET film prepared in Example 1A, with the primer layer facing the Ni mold using a GBC Eagle 35 laminator (GBC, Northbrook, IL) preset at a roller temperature of 100°C, lamination speed of 1 ft/min and the roll gap at "heavy gauge". A UV curing station with a UV intensity of 2.5 mJ/cm<sup>2</sup> was used to cure the panel for 5 seconds. The ITO/PET film was then peeled away from the Ni mold at a peeling angle of about 30 degree to give a 4"x4" microcup array on ITO/PET. An acceptable release of the microcup array from the mold was observed. The thus obtained microcup array was further post-cured with a UV conveyor curing system (DDU, Los Angeles, CA) with a UV dosage of 1.7 J/cm<sup>2</sup>.

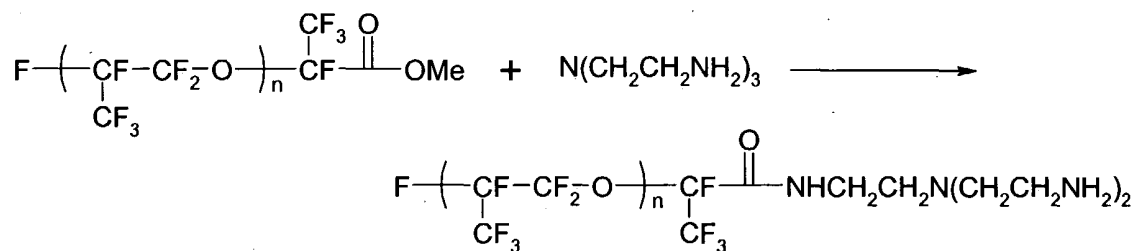
#### **Example 1C:**

##### **Preparation of Electrophoretic Fluid**

[0103] 5.9 Gm of TiO<sub>2</sub> R900™ (DuPont) was added to a solution containing of 3.77 gm of MEK, 4.54 gm of N3400™ aliphatic polyisocyanate (Bayer AG) and 0.77 gm of 1-[N,N-bis(2-hydroxyethyl)amino]-2-propanol (Aldrich). The resultant slurry was homogenized for 1 minute at 5-10°C, after which 0.01 gm of dibutyltin dilaurate (Aldrich) was added and the mixture was homogenized for an additional minute. Finally a solution containing 20 gm of HT-200™ (Ausimont, Thorofare, NJ) and 0.47 gm of Rf-amine4900 [a precondensate of Krytox methyl ester (from Du

Pont) and tris(2-aminoethyl)amine (Aldrich) prepared as shown below] was added and the mixture was homogenized again for 3 more minutes at room temperature.

[0104] The Rf-amine4900 was prepared according to the following reaction:



(Rf-amine4900; n= about 30)

[0105] The slurry prepared above was added slowly over 5 minutes at room temperature under homogenization into a mixture containing 31 gm of HT-200 and 2.28 gm of Rf-amine4900. The resultant TiO<sub>2</sub> microcapsule dispersion was stirred under low shear with a mechanical stirrer at 35°C for 30 minutes, then heated to 85°C to remove MEK and post cure the internal phase for three hours. The dispersion showed a narrow particle size distribution ranging from 0.5-3.5 microns. The slurry was diluted with equal amount of PFS-2<sup>TM</sup> (Ausimont, Thorofare, NJ) and the microcapsules were separated by centrifuge fractionation to remove the solvent phase. The solid collected was washed thoroughly with PFS-2<sup>TM</sup> and redispersed in HT-200.

#### Example 1D:

##### Filling and Sealing with a Sealing Composition

[0106] 1 Gm of an electrophoretic composition containing 6 parts (based on dry weight) of the TiO<sub>2</sub> microparticles prepared above and 94 parts of a HT-200 (Ausimont) solution of 1.5 wt% of a perfluorinated Cu-phthalocyanine dye (FC-3275, 3M, St. Paul, MN) was metered into the 4"x4" microcup array prepared from Example 1B. The excess of fluid was scraped away by a rubber blade. The filled microcups were then overcoated with a 10% rubber solution consisting of 9 parts



of Kraton G1650 (Shell, TX), 1 part of GRP 6919 (Shell), 3 parts of Carb-O-Sil TS-720 (Cabot Corp., IL), 78.3 parts of Isopar E and 8.7 part of isopropyl acetate by a Universal Blade Applicator and dried at room temperature to form a seamless sealing layer of about 2-3  $\mu\text{m}$  dry thickness with good uniformity.

**Example 1E:**

**Lamination**

[0107] The ITO side of an ITO/PET conductor film (5 mil OC50 from CPFilms) was overcoated with a 25 wt% solution of a pressure sensitive adhesive (Durotak 1105, National Starch, Bridgewater, NJ) in methyl ethyl ketone (MEK) by a Myrad bar (targeted coverage: 0.6 gm/ft<sup>2</sup>). The adhesive coated ITO/PET layer was then laminated over the sealed microcups prepared from Example 1D with a GBC Eagle 35 laminator at 70°C. The lamination speed was set at 1ft/min with a gap of 1/32". The thus prepared EPD panel showed a contrast ratio of 1.5 at  $\pm 20$  V against a black background.

### **Example 2**

[0108] The procedure of Example 1 was repeated, except that the sealing layer (Example 1D) and the adhesive layer (Example 1E) were replaced by those of Examples 2A and 2B respectively.

### **Example 2A:**

#### **Sealing Layer Composition Containing Carbon Black**

[0109] 27.8 Gm of carbon black (Vulcan™ XC72, Cabot Corp.) was dispersed thoroughly into 320 gm of an isopropyl acetate/Isopar E (1/9) solution containing 0.75 wt% of Disperse-Ayd 6 (Elementis Specialties) using a high-speed disperser (Powergen, model 700 equipped with a 20 mm-saw-tooth shaft). A 10% (by weight) rubber solution (80 gm) containing 9 parts of Kraton™ G1650, 9 parts of Kraton™ RPG6919 (from Shell Chemical), 1 part of Isopropyl acetate and 81 parts of Isopar-E was added into the carbon black dispersion and mixed for another 30 minutes. The resultant carbon black dispersion was mixed with an additional 1780 gm of the same 10% rubber (Kraton™ G1650/Kraton™ RPG6919=9/1) solution, homogenized using a Silverson L4RT-A homogenizer for 2 hours and filtered through a 40µm filter.

### **Example 2B:**

#### **Adhesive Layer Composition Containing a Dye**

[0110] A solution containing of 6.0 gm of a 25 wt% solution of Orasol™ BlueGL (Ciba Specialty Chemicals, High Point, NC) in MEK, 20.0 gm of Duro-Tak™ 80-1105 adhesive (50% solid from National Starch, Bridgewater, NJ) and 51.0 gm of MEK was coated onto the ITO side of an ITO/PET film and laminated onto the sealed microcup array containing the electrophoretic fluid as prepared in Example 1. The target coverage of the adhesive remains the same: 0.6 gm/ft².

[0111] The EPD panel showed a contrast ratio of 6.2 at ±20V.

### Examples 3 to 7

[0112] The procedure of Example 2 was followed, except that the Orasol™ Blue GL was replaced with the different dyes in the adhesive layer as shown in Table 1.

**Table 1 Effect of Dyes and Carbon Black in Adhesive and Sealing Layers**

	Additive in Adhesive Layer	Additive in Sealing Layer	Contrast Ratio at $\pm 20$ V	Contrast Ratio at $\pm 30$ V
Comparative Example 1	None	None	1.5	2.2
Example 2	13 wt% Orasol Blue GL	13 wt% Carbon Black	6.2	9.3
Example 3	13 wt% Orasol Red BL	13 wt% Carbon Black	6.0	8.5
Example 4	13 wt% Orasol Yellow 2GLN	13 wt% Carbon Black	5.5	8.2
Example 5	13 wt% Orasol Black CN	13 wt% Carbon Black	5.2	8.1
Example 6	13 wt% Orasol Black RLI	13 wt% Carbon Black	5.0	7.2
Example 7	13 wt% Sudan Black	13 wt% Carbon Black	5.0	6.7

[0113] All the Orasol™ dyes in Table 1 were obtained from Ciba Specialty Chemicals, and the Sudan Black was obtained from Aldrich.

### **Example 8**

[0114] The procedure of Example 2 was followed, except that the Orasol™ BlueGL in the adhesive layer was replaced with barium titanate ( $\text{BaTiO}_3$ ). Thus, 12 gm of barium titanate (K-Plus-16, from Cabot, MA) was dispersed using a sonicator (Fisher dismembrator, Model 550) into the adhesive solution containing 15.5 g of Duro-Tak™ 80-1105, 18.8 gm of ethyl acetate, 15.9 gm of toluene, 1.4 gm of hexane and 1.1 gm of a polymeric dispersant (Disperbyk 163, BYK Chemie). The adhesive was coated onto the ITO side of an ITO/PET film (targeted dry coverage: 6 mm) and the resultant film was laminated onto the sealed microcup array as in Example 2 at 100°C.

[0115] The EPD panel showed a contrast ratio of 6.1 at  $\pm 30\text{V}$ .

### **Comparative Example 9**

[0116] The procedure of Example 8 was followed, except that no  $\text{BaTiO}_3$  was used in the adhesive layer (target dry coverage: 6  $\mu\text{m}$ ).

[0117] The EPD panel showed a contrast ratio of 4.7 at  $\pm 30\text{V}$ .

### **Example 10**

[0118] The procedure of Example 2 was followed, except that the Orasol™ BlueGL in the adhesive layer was replaced with N,N'-(bis(3-methylphenyl)-N,N'-diphenylbenzidine (BMD). Thus, 0.42 gm of BMD was dissolved at 80°C into 28 gm of a 10 wt% solution of adhesive Duro-Tak™ 80-1105 in dimethyl formamide (DMF). The resultant adhesive solution was coated on the ITO side of a 5-mil ITO/PET using wire bars #12 and the resultant film was laminated onto the sealed microcup array as in Example 2 at 100°C.

[0119] The EPD panel showed a contrast ratio of about 3 at  $\pm 20\text{V}$ .

### **Comparative Example 11**

**[0120]** The procedure of Example 10 was followed, except that no BMD was used in the adhesive layer. The EPD panel thus prepared showed a contrast ratio of about 2 at  $\pm 20\text{V}$ .

**[0121]** While the present invention has been described with reference to the specific embodiments thereof, it should be understood that various changes may be made and equivalents may be substituted without departing from the true spirit and scope of the invention. In addition, many modifications may be made to adapt a particular situation, materials, compositions, processes, process step or steps, to the objective, spirit and scope of the present invention. All such modifications are intended to be within the scope of the claims appended hereto.